

A NOTE ON THE APPLICATION OF THE GLASS  
ELECTRODE TO THE DETERMINATION OF  
OXIDATION-REDUCTION POTENTIALS

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The electromotive force of the chain consisting of a glass electrode and a bare noble metal is influenced by the presence of oxidation-reduction systems in the solution. It has been frequently stated that such an electrode system may be used to determine oxidation-reduction potentials independently of simultaneous effects of pH, but this statement must be extensively qualified, as will be seen from the following discussion.

Ignoring the small asymmetry potential existing between the two glass surfaces, there are four sources of electrical activity in the chain. They are the half cell inside the glass electrode, the liquid-glass interface potential on the inner surface of the glass, the glass-liquid interface potential on the outer surface of the glass, and the oxidation-reduction potential imparted to the platinum. Any solution containing an oxidation-reduction system in which the glass electrode and the platinum electrode are immersed will affect the electromotive force of the chain in two ways. The oxidation-reduction system will impart a potential to the platinum, and the hydrogen ions present will modify the glass-liquid interface potential on the outer surface of the glass.

If the pH of the solution remains constant, then only changes in the oxidation-reduction potential will modify the E.M.F. of the chain. The true  $E_h$  of the oxidation-reduction system may be calculated by applying a calibration correction obtained by observing the E.M.F. of the chain when immersed in some known system at the same pH as that of the unknown

system. If the pH of the solution changes during the course of oxidation-reduction potential measurement, either of two conditions may exist. A consideration of the formula is necessary for their explanation:

$$E_h = E_o - \frac{RT}{nF} \ln \frac{(\text{reductant})}{(\text{oxidant})} - \frac{RT}{nF} \ln \frac{(\text{reductant})}{(\text{oxidant})} - \frac{RT}{nF} \ln \frac{K_a}{(H^+) + K_a}$$

The oxidation-reduction potential is seen to be a function of the ratio of total reductant to total oxidant, and also of pH.

First, if the system is such that the slope of the curve relating changes in pH to changes in oxidation-reduction potential is the same as that relating changes in pH to changes of the glass-liquid interface potential, then these two effects of pH cancel each other and the potentials of the system would correspond to those obtained at a constant pH. It is this that has given rise to the statement that the glass electrode records oxidation-reduction potential independently of pH changes. The falsity of this view comes from the fact that the observed reading must be corrected by an empirical factor obtained by observing the potential given by a known oxidation-reduction system at the same pH as that of the unknown. The magnitude of this calibration correction *changes* with pH, and hence its application to the observed reading will not give the  $E_h$  of the solution if the pH has changed from that of the calibrating system. In order to obtain the true  $E_h$  of a system of changing pH, determinations of pH must be made simultaneously with those of oxidation-reduction potential, from which new calibration corrections can be calculated.

On the other hand, if the system is such that the slope of the curve relating changes in pH to changes in oxidation-reduction potential is unlike that relating changes of pH on the glass-liquid interface potential, then the two effects of pH do not cancel each other. In order to convert observed potentials to  $E_h$  one would need to take simultaneous measurements of pH changes, and then apply as a correction factor only that part of the pH effect that is cancelled by the response of the glass electrode to the same pH changes. This would be a complicated

and tedious process—and only possible if the reaction of the redox system to changes in acidity were accurately known. Clark and Cohen<sup>1</sup> were the first to point out the various theoretically possible relationships between pH and oxidation-reduction potentials. They show how very complex is the effect of pH on many oxidation-reduction systems. For this reason, it is impossible to use this chain to determine the  $E_n$  of such complex biological systems as growing bacterial cultures, if the pH is changing simultaneously.

The use of the glass electrode in the determination of oxidation-reduction potentials is limited to buffered solutions, and its advantage lies solely in its high resistance and consequent lack of polarization. A high resistance (10 megohms) inserted in the usual calomel-platinum chain would be equally advantageous.

It may be pointed out that if the potential of the oxidation-reduction system changes with pH to the same degree as does the glass-liquid interface potential, then the observed E.M.F. of the oxidation-reduction system will be in terms of the pH *inside* the glass electrode. This apparently anomalous phenomenon has a simple explanation.

If the outside solution contains no oxidation-reduction system and is at the same pH as the fluid inside the glass electrode, then, ignoring the asymmetry potential, the potentials on the glass surfaces cancel each other, since they are functions of pH and are exerted in opposite directions. Again, for simplicity, ignoring certain possible ionic effects on the platinum, there remains in the chain but a single effective source of electromotive force, the half cell inside the glass electrode. Since a single source of electrical potential cannot be measured, there will be no E.M.F. detected in the system. Now, if quinhydrone be added to the outer liquid, a potential will be imparted to the platinum whose magnitude in comparison with the normal hydrogen electrode will be defined by the equation given above.

<sup>1</sup> Clark, W. M., and Cohen, B. Studies on oxidation-reduction. II. An analysis of the theoretical relations between reduction potentials and pH. U. S. Public Health Reports 38: 666–683. 1923.

The effective sources of electromotive force in the glass electrode-platinum chain consist of only the half cell inside the glass electrode and the oxidation-reduction potential imparted to the platinum, since the interface potentials on the glass surfaces cancel each other. The potential of the half cell inside of the glass electrode can be expressed in terms of the normal hydrogen electrode ( $E_h$ ) by applying a suitable correction, and then the system reads the  $E_h$  of the oxidation-reduction system in terms, of course, of the pH, which under the conditions defined above is the same on both sides of the glass.

Now, if the pH of the solution in which the oxidation-reduction system is dispersed is changed by one pH unit, then the oxidation-reduction potential on the platinum changes by 59 millivolts (at 25° C.). However, this effect on the electromotive force of the oxidation-reduction system is the same quantitatively as that on the glass-liquid interface potential. These effects, therefore, cancel each other and the total E.M.F. of the chain will read as before. If the original pH equals 1.00 on both sides of the glass membrane, then it can be seen that no matter how the pH of the oxidation-reduction system outside be changed, the reading will still represent the  $E_h$  of the system at pH = 1.00. But if the pH outside the glass electrode remains at 1.00, and the pH inside is changed by 1 pH unit, the pH effect is no longer cancelled and the total E.M.F. of the chain will change 59 millivolts. The chain again does not indicate the  $E_h$  of the oxidation-reduction system, since that obviously has not changed. But the magnitude of this change, which is the pH effect on the inner surface of the glass, is the same as the change of oxidation-reduction potential if it were varied by this same pH unit.

It is now clear that the observed potential of all oxidation-reduction systems which vary 59 millivolts with a change of acidity of one pH unit will depend on the pH inside of the glass electrode, and curiously enough not that of the liquid in which the system is actually dispersed.

The validity of the above discussion depends on the assumption that the half cell inside the glass electrode is a metal in

equilibrium with its ions such as  $\text{Ag}:\text{AgCl}$  or  $\text{Hg}:\text{HgCl}$ . If this electrode is a noble metal in equilibrium with an oxidation-reduction system, e. g., platinum:quinhydrone, then the observed potential of the system will be the difference in millivolts between the oxidation-reduction potentials of the system inside and that outside the glass electrode, both dispersed in solutions of equal hydrogen ion concentration. Reconsideration of the above discussion will show that this will be true regardless of how the actual pH of the two solutions differ from each other, providing only that the pH of each is such that both systems vary 59 millivolts per pH unit change.